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L4: Entry 17 of 26 File: USPT Jun 27, 2000

DOCUMENT-IDENTIFIER: US 6080526 A

TITLE: Integration of low-k polymers into interlevel dielectrics using controlled

electron-beam radiation

Brief Summary Text (9):

It has now been discovered that the properties of certain spin-on <u>dielectric</u> films used in IC interconnect processing are improved when those films are cured with a controlled <u>electron</u> beam radiation <u>treatment</u> when compared to a thermal cure. Thus, for example, the invention provides improved methods for achieving non-etchback process for spin-on low-k <u>dielectrics</u> using controlled <u>electron</u> beam radiation processes. The invention also provides improved methods for protecting the underlying <u>dielectric</u> layer from process environment induced degradation, particularly <u>dielectric</u> constant of certain spin-on low-k polymer films using a controlled <u>electron</u> beam radiation process. The invention also provides improved methods for retaining the intrinsic <u>dielectric</u> constant for spin-on polymer films in areas such as in between metal lines using controlled <u>electron</u> beam radiation process.

Brief Summary Text (10):

It has been discovered that if a freshly deposited spin-on dielectric film is exposed to an electron beam radiation under relative low energy conditions, subsequent to standard hotplate treatments, then a "skin" is formed as the outer layer of the film which has been most directly contacted by the electron beam radiation. The thickness of this "skin" can be regulated by the electron beam energy levels, including the time duration of exposure, and the integrated (total) electron beam dosage delivered to the film. Thus, the film can be only lightly cured such that a thin skin of nominally 500-6000 angstroms can be formed, depending on the interlayer dielectric thickness. A continuum of extents of cure for the films can be thus be advantageously used in semiconductor processing. A relatively brief cure in which a skin is formed simultaneously allows retention of the low dielectric constant of the film, attainment of a hardened, oxidation resistant outer layer on the film, and minimization of process time when compared to the electron beam radiation cure of the full thickness of the film. With this process, the original homogeneous dielectric layer can be converted into two distinctive layers. The dielectric layer on the top of metals is significantly modified and thus some of its properties have been significantly changed. This layer has such excellent properties as low or no moisture absorption and low or no degradation upon exposure to high temperature and oxygen plasma environments, and thus a non-etchback process can be achieved without degradation. The underlying dielectric layer, particularly in between-metal lines, retains its intrinsic dielectric properties such as low dielectric constant. The modified top layer protects the underlying dielectric layer and thus the properties of the underlying dielectric is not affected by high temperature and oxygen plasma exposure.

Detailed Description Text (34):

Silicon wafers were coated using conventional spin-coating with a solution comprising either a methyl silsesquioxane polymer and a mixture of organic solvent or a hydrogen silsesquioxane polymer and a mixture of organic solvent. The coated wafers were subjected to successive hot plate treatments followed by either thermal curing, partial e-beam curing or full e-beam curing. Table 4 shows the conditions for this experiment with detailed conditions for bake, thermal cure and e-beam cure. Aluminum dots with thickness of about 1 micron and diameter of 0.5 mm were coated on

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L4: Entry 18 of 26

File: USPT

Mar 28, 2000

DOCUMENT-IDENTIFIER: US 6042994 A

TITLE: Nanoporous silica dielectric films modified by electron beam exposure and having low dielectric constant and low water content

Abstract Text (1):

Nanoporous silica <u>dielectric</u> films are modified by <u>electron beam</u> exposure after an optional hydrophobic <u>treatment</u> by an organic reactant. After formation of the film onto a substrate, the <u>substrate</u> is placed inside a large area <u>electron beam</u> exposure system. The resulting films are characterized by having a low <u>dielectric constant</u> and low water or silanol content compared to thermally cured films. Also, e-beam cured films have higher mechanical strength and better resistance to chemical solvents and oxygen plasmas compared to thermally cured films.

Brief Summary Text (9):

Thus, it would be desirable to produce a nanoporous silica film which has a dielectric constant .ltoreq.2.5, which contains low levels of water and which is stable to oxygen plasma as well as to other chemical solvents used in IC fabrication This can be accomplished in accordance with this invention, wherein nanoporous silica dielectric films are modified by electron beam exposure after an optional hydrophobic treatment by an organic reactant. The resulting films retain their nanoporous structures with reduced pore sizes, and initially have lower water content compared to thermally cured films, and hence have a dielectric constant lower than or the same as that of the thermally cured films. The resulting films have essentially no or a reduced amount of carbon and hydrogen after the electron beam process. These electron beam treated films are also not affected by oxygen plasma and chemical solvents, such as used in IC fabrication. The resistance to oxidizing plasma and chemical solvents results from the absence of methyl groups in the film as well as because of e-beam induced densification. Without the electron beam process, the oxygen plasma would react with the trimethylsilyl groups to form water. The water would raise the dielectric constant of the film and lead to high leakage current between metal lines. Although it has been previously suggested to form hydrophobic nanoporous films by treating the film with an organic surface modification reagent, the benefits of exposing such films to an electron beam were heretofore not known. Such prior art is exemplified by U.S. Pat. Nos. 5,494,858; 5,504,042; 5,523,615; and 5,470,802, as well as Ramos, et. al, "Nanoporous Silica for Dielectric Constant Less Than 2, ULSI Meeting, Boston, Mass., October 1996; Ramos, et. al, "Nanoporous Silica for ULSI Applications", 1997 Dielectrics for ULSI Multilevel Interconnection Conference (DUMIC), P. 106; and Jin, et. al., "Porous Xerogel Films as Ultra-Low Permittivity Dielectrics for ULSI Interconnect Applications", ULSI Meeting, Boston Mass., October 1996.

Detailed Description Text (26):

After formation of the nanoporous film which may or may not have been treated with the surface modifying agent, the substrate is placed inside the chamber of a large area electron beam exposure system, such as that described in U.S. Pat. No. 5,003,178 to Livesay, the disclosure of which is incorporated herein by reference. This apparatus exposes the entire substrate to an electron beam flux all at once. The electron beam exposure is done at a vacuum in the range of from about 10.sup.-5 to about 10.sup.2 torr, and with a substrate temperature in the range of from about 25.degree. C. to about 1050.degree. C. The electron energy and doses will fall into the ranges of about 0.5 to about 30 KeV and about 500 to about 100,000 .mu.C/cm.sup.2, respectively. The nanoporous dielectric is subjected to an electron